



TITLE:

First synthesis of fullerene trimer C<sub>180</sub> and its structural identification by scanning tunnelling microscopy(STM)/  
Synthesis of novel derivatives of fullerene dimers and open-cage fullerene (ORGANIC MATERIALS CHEMISTRY - High-Pressure Organic Chemistry)

AUTHOR(S):

KOMATSI, Koichi; KITAGAWA, Toshikazu; MORI, Sadayuki; NISHINAGA, Tohru; MURATA, Yasujiro; CHENG, Fuyong

---

CITATION:

KOMATSI, Koichi ...[et al.]. First synthesis of fullerene trimer C<sub>180</sub> and its structural identification by scanning tunnelling microscopy(STM)/ Synthesis of novel derivatives of fullerene dimers and open-cage fullerene (ORGANIC MATERIALS CHEMISTRY - High-Pressure Organic Chemistry). ICR Annual Report 2002, 8: 32-33

ISSUE DATE:

2002-03

URL:

<http://hdl.handle.net/2433/65316>

RIGHT:

## Organic Materials Chemistry -High-Pressure Organic Chemistry-



Prof  
KOMATSU, Koichi  
(D Eng)



Assoc Prof  
KITAGAWA, Toshikazu  
(D Eng)



Instr  
MORI, Sadayuki  
(D Eng)



Instr  
NISHINAGA, Tohru  
(D Eng)



Instr  
MURATA, Yasujiro  
(D Eng)



Guest Res Assoc  
CHENG, Fuyong  
(D Sc)

### Students

FUJIWARA, Koichi (D3)  
LEE, Yangsoo (D1)  
KONNO, Hirofumi (M2)  
IDOMOTO, Yuichi (M1)  
MURATA, Michihisa (M1)  
YAMAZAKI, Daisuke (RS)

WAKAMIYA, Atsushi (D2)  
INOUE, Ryota (M2)  
SUZUKI, Mitsuharu (M2)  
MIYATA, Yasuo (M1)  
MASAOKA, Naoki (UG)

### Visitor

Prof WANG, Guan-Wu

University of Science and Technology of China, 1 July 2001 - 31 August 2001

## Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties. The major subjects are: synthetic and structural studies on novel cyclic  $\pi$ -conjugated systems, particularly the positively charged species stabilized by  $\sigma$ - $\pi$  interaction; synthesis of new redox-active and supramolecular  $\pi$ -systems; organo-chemical transformation of fullerene  $C_{60}$ , specifically the synthesis of fullerene dimers and trimers by the use of mechanochemical solid-state reactions; synthesis and reactions of open-cage fullerene derivatives; generation of alkylated  $C_{60}$  cation and its application for synthesis of functional materials.

## Research Activities (Year 2001)

### Presentations

Synthesis of the first planar COT annelated with bicyclo[2.1.1]hexene, Komatsu K, Matsuura A, International Symposium on Novel Aromatics, 5 August.

Generation and properties of the first alkylated  $C_{60}$  cations, Kitagawa T, Takeuchi K, Komatsu K, et al., International Symposium on Novel Aromatics, 5 August; International Symposium on Reactive Intermediates and Unusual Molecules, 13 September.

Synthesis of the fullerene trimer  $C_{180}$  and its STM observation, Komatsu K, Kunitake M (Kumamoto), Ito O (Tohoku), et al., Japan-Israel Binational Symposium on the Functional Supramolecular Materials, 16 October.

Synthesis and  $\sigma$ - $\pi$  interaction of cyclic  $\pi$ -conjugated molecules annelated with bicyclic frameworks, Komatsu K, Nishinaga T, et al., Kyushu International Symposium on Physical Organic Chemistry, 28 November.

### Grants

Komatsu K, Design and synthesis of  $\pi$ -electronic and related cationic systems having  $\sigma$ - $\pi$  interaction, Grant-in-Aid for Scientific Research on Priority Areas (A) (2), 1 April 2000 - 31 March 2002.

Kitagawa T, Development of the method of alkylating  $C_{60}$  by way of alkylfullerenyl cation, Grant-in-Aid for Scientific Research (C) (2), 1 April 2000 - 31 March 2002.

Nishinaga T, Synthesis and properties of sulfur-containing cyclic  $\pi$ -electronic systems annelated with bicyclic frameworks, Grant-in-Aid for Encouragement of Young Scientists (A), 1 April 2000 - 31 March 2002.

Murata Y, Transformation of fullerene  $C_{60}$  using mechanochemical high-speed vibration-milling technique, Grant-in-Aid for Encouragement of Young Scientists (A), 1 April 2000 - 31 March 2002.

## Topics

### First synthesis of fullerene trimer $C_{180}$ and its structural identification by scanning tunnelling microscopy (STM)

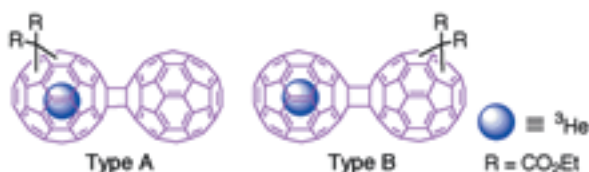
The fullerene dimer and trimer are the most essential subunits of the all-carbon fullerene polymers. The mechanochemical solid-state reaction of fullerene  $C_{60}$  catalyzed by 4-aminopyridine was found to give not only the dimer  $C_{120}$  but also the trimer  $C_{180}$  albeit in a low yield (4%). The HPLC analysis indicated that  $C_{180}$  consists of several structural isomers. These isomers were separated into two fractions, I and II, which were supposed to have the extended / folded structures and a cyclic structure, respectively, based on the HPLC absorption behavior and theoretical calculations. This supposition was proved by the first direct STM observation of actual images of individual isomers as shown in the figure.[1]

1. Kunitake M, Uemura S, Ito O, Murata Y, Fujiwara K, Komatsu K, *Angew. Chem. Int. Ed.*, in press.

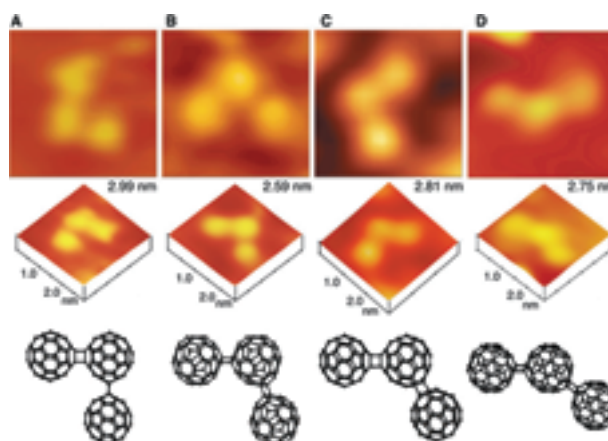
### Synthesis of novel derivatives of fullerene dimers and an open-cage fullerene

The solid-state and the liquid-phase thermal reactions of fullerene  $C_{60}$  with 2, 3-diazanaphthalene afforded, respectively, the  $C_{60}$  dimers incorporated in a bicyclic framework (shown in silver) and a benzo-derivative of an open-cage fullerene (shown in gold) in the figure.[1] The orifice of the latter was further enlarged to a 12-membered ring by the photochemical oxidation with singlet oxygen, thus suggesting the possibility of organic synthesis of endohedral fullerenes.[2]

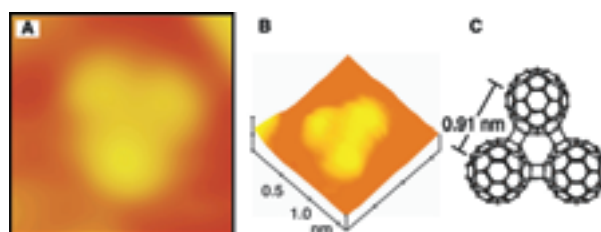
On the other hand, the directly connected fullerene dimer  $C_{120}$  containing  $^3\text{He}$  in one of the cages was synthesized by solid-state reaction, and its cyclopropanation reaction was examined. Based on the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^3\text{He}$  NMR analysis on the products carefully separated by HPLC, the isomer distribution of the two types of products (A and B, shown below) was clarified. It was proved that the reactivity of the  $C_{60}$  cage is not affected by incorporation of the He atom and there is appreciable magnetic interaction between the two cages.[3]



1. Murata Y, Kato N., Komatsu K, *J. Org. Chem.*, **66**, 7235 (2001).
2. Murata Y, Komatsu K, *Chem. Lett.*, **2001**, 896.
3. Fujiwara K, Komatsu K, Wang G-W, Tanaka T, Hirata K, Yamamoto K, Saunders, M., *J. Am. Chem. Soc.*, **123**, 10715 (2001).



STM images of fraction I



STM images of fraction II

